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DESENSITIZATION OF EXPLOSIVE MATERIALS

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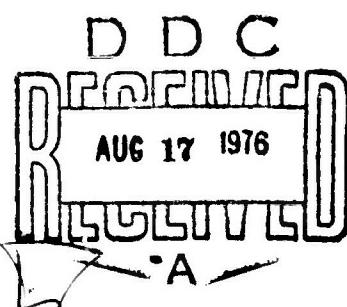
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AB

INTRODUCTION AND SUMMARY

The objective of our work is to determine the generality of an observation that substitution of fluorine for hydrogen in an explosive material leads to desensitization. Substitution of the $-\text{CH}_2-$ group in FEFO, $[\text{FC}(\text{NO}_2)_2\text{CH}_2\text{O}]_2\text{CH}_2$, with a $-\text{CF}_2-$ group to give DFF, $[\text{FC}(\text{NO}_2)_2\text{CH}_2\text{O}]_2\text{CF}_2$, reduces the sensitivity to impact and low velocity detonation (LVD). In addition to having reduced sensitivity, DFF has higher density and lower melting point than FEFO.¹ To generalize our hypothesis that the substitution of fluorine for hydrogen will desensitize an explosive, first we are preparing formals analogous to FEFO and DFF and determining their sensitivity characteristics to be followed by fluorine analogs of explosive nitrate esters, heterocyclics and other classes.

In this report period, $[\text{C}(\text{NO}_2)_3\text{CH}_2\text{O}]_2\text{CF}_2$, compound 8,[†] was prepared for comparison with $[\text{C}(\text{NO}_2)_3\text{CH}_2\text{O}]_2\text{CH}_2$, compound 7. Also, the synthesis of HADDF, $[\text{FC}(\text{NO}_2)_2\text{CH}_2\text{OCH}_2\text{OCH}_2]_2\text{C}(\text{NO}_2)_2$, compound 13, was begun for comparison of the chemical and physical properties with ADDF, $[\text{FC}(\text{NO}_2)_2\text{CH}_2\text{OCF}_2\text{OCH}_2]_2\text{C}(\text{NO}_2)_2$, compound 14.

¹J. M. Guimont and H. M. Peters, "Desensitization of Explosive Materials", Monthly Report No. 1, July 2, 1976.

[†]Numbers refer to compounds listed in Table 1.

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Table 1
LINEAR FORMALS AND DIFLUOROFORMALS

Compound	No.	(RO) ₂ CH ₂ (Formals)		(RO) ₂ CF ₂ (Fluoroformals)		
		Structure		Compound	No.	Structure
FEFO	1	[FC(NO ₂) ₂ CH ₂ O] ₂ CH ₂	*	DFF	2	[FC(NO ₂) ₂ CH ₂ O] ₂ CF ₂
DNPF	3	[H ₃ CC(NO ₂) ₂ CH ₂ O] ₂ CH ₂	*	NPFF	4	[H ₃ CC(NO ₂) ₂ CH ₂ O] ₂ CF ₂
TDPF	5	[CF ₃ OCH ₂ C(NO ₂) ₂ CH ₂ O] ₂ CH ₂	*	OTT	6	[CF ₃ OCH ₂ C(NO ₂) ₂ CH ₂ O] ₂ CF ₂
TEFO	7	[C(NO ₂) ₃ CH ₂ O] ₂ CH ₂	*	#	8	[C(NO ₂) ₃ CH ₂ O] ₂ CF ₂
#	9	FC(NO ₂) ₂ CH ₂ OCH ₂ OCH ₂ C(NO ₂)F ₂	*	MFF	10	FC(NO ₂) ₂ CH ₂ OCH ₂ C(NO ₂)F ₂
#	11	FC(NO ₂) ₂ CH ₂ OCH ₂ OCH ₂ CF ₃	*	TMFF	12	FC(NO ₂) ₂ CH ₂ OCH ₂ OCH ₂ CF ₃
#	13	[FC(NO ₂) ₂ CH ₂ OCH ₂ OCH ₂] ₂ C(NO ₂) ₂	*	ADDF	14	[FC(NO ₂) ₂ CH ₂ OCH ₂ OCH ₂] ₂ C(NO ₂) ₂
#	15	FC(NO ₂) ₂ CH ₂ OCH ₂ CH ₂ OCH ₂ C(NO ₂) ₂ F	*	HTD	16	FC(NO ₂) ₂ CH ₂ OCH ₂ CF ₂ OCH ₂ C(NO ₂) ₂ F

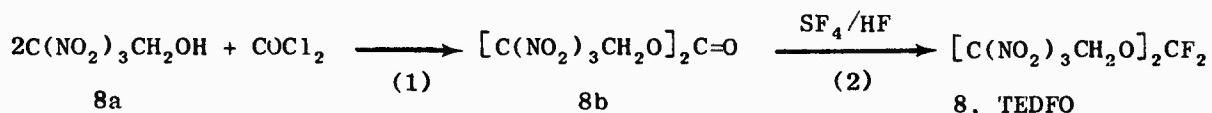
* Site of change.

† Not previously reported.

DISCUSSION OF RESULTS

Comparison of $[C(NO_2)_3CH_2O]CF_2$, compound 8, with $[C(NO_2)_3CH_2O]CH_2$, compound 7 (TEFO)

We prepared bis(trinitroethyl) difluoroformal, compound 8, by the route shown in Eqs. 1 and 2.



The carbonate, 8b, prepared during the previous report period, was fluorinated in a high pressure reactor using sulfur tetrafluoride with anhydrous hydrofluoric acid as catalyst and solvent. The results of the five trials are shown in Table 2. Based on our previous experience with sulfur tetrafluoride, we expected the reaction temperature to be the most critical parameter. The results of trials 2, 4, and 5 showed that reaction temperature is important but that other parameters may be equally so. Since the conditions of trial 5 produced about 75% conversion to the desired product, 8, we plan to force the reaction to completion by repeating trial 5 at 105°C on a larger scale using a longer reaction time.

A complete physical property determination of compound 8 is in progress.

Comparison of ADDF with HADDF

We also began the synthesis of the hydrocarbon analog (HADDF, compound 13) of ADDF for comparison of sensitivity properties. In one approach, fluorodinitroethylchloromethyl ether was treated with 2,2-dinitropropane-1,3-diol in the presence of stannic chloride as catalyst, Eq. 3.

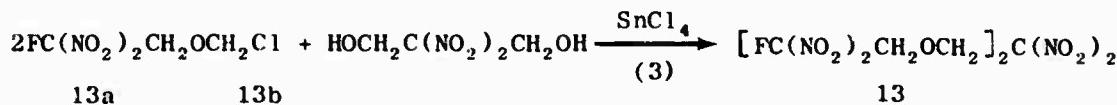


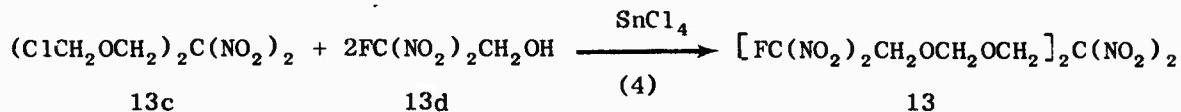
Table 2
 $\left[\text{C}(\text{NO}_2)_3 \text{CH}_2\text{O} \right]_2 \text{C=O} \rightarrow \left[\text{C}(\text{NO}_2)_3 \text{CH}_2\text{O} \right]_2 \text{CF}_2$

Trial	Carbonate (g/mmol)	HF mmol	SF ₄ mmol	Temp. °C	Time hrs	Product (g)	Remarks*
1	10/48	100	157	90	20	9.5	Starting material recovered
2	10/48	1100	102	90	20	9.2	Starting material recovered
3	10/48	1300	74	120	20	9.2	Starting material plus small amount product
4	10/48	1300	102	120	120	0.8	Primarily decomposition
5	10/48	1100	194	105	72	9.4	75% Product, 25% starting material

*Product identification is based on ir and nmr analyses.

The mixture of reaction products is currently undergoing separation and identification.²

Similarly in a second approach, 1,3-bis(chloromethyl)-2,2-dinitropropyl ether was treated with fluorodinitroethanol Eq. 4.



Again, a mixture of products was obtained. Although bis(fluorodinitroethyl) formal, $[\text{FC}(\text{NO}_2)_2\text{CH}_2\text{O}]_2\text{CH}_2$, and 5,5-dinitro-1,3-dioxane, $(\text{NO}_2)_2\text{C}\overline{\text{CH}}_2\text{OCH}_2\text{OCH}_2$, have been identified as reaction products of both attempted reactions, the presence of Compound 13 has not yet been confirmed. The product analyses of the two reactions, Eq. 3 and 4, have not been completed and are continuing because we believe that some of compound 13 was formed and can be isolated. Other workers have obtained mixtures from chloromethyl ether reactions with similar electronegatively substituted alcohols.³

²G. W. Lawrence, L. E. Kayser, and H. G. Adolph, "ALWT - High Energy Plasticizer and Binder Synthesis", Final Report, February 15, 1976.

³H. G. Adolph and M. J. Kamlet, J. Org. Chem., 34, 45 (1969).

FUTURE WORK

During the next report period we plan to characterize and prepare in quantity $[C(NO_2)_3CH_2O]_2CF_2$, compound 8, and begin testing its sensitivity for comparison with compound 7 (impact, hVD, LVD).

We also plan to complete the characterization of the products of the chloromethyl ether reactions, Eq. 3 and 4, and to continue our investigation of the synthesis of compound 13, $[FC(NO_2)_2CH_2OCH_2OCH_2]_2C(NO_2)_2$.

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Trinitroethyl difluoroformal (TEDFO)

Replacement C-H by C-F

Reduced low velocity detonation (LVD)

High Velocity Detonation (HVD)

Impact Sensitivity

ADDF versus -CH₂- ADDF

20 ABSTRACT (Continued)

The generalize hypothesis that the substitution of fluorine for hydrogen will desensitize an explosive, first we are preparing formals analogous to FEFO and DFF and determining their sensitivity characteristics. to be followed by fluorine analogs of explosive nitrate esters, heterocyclics and other classes.

* are being prepared

* This research will continue on